**Chemistry Notes: Chemical Kinetics**

**Kinetics** - deal with how and how fast a reaction occurs; it has nothing to do with the extent to which a reaction will occur; the extent is governed by thermodynamics.

As we will see, there are several factors which affect the rate of a chemical reaction including:

1. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

2. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

3. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

4. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**Reaction Rates** : How can we define a rate of a reaction?

**Rate** = Δ concentration/Δtime = Δ[product]/Δt = -Δ[reactant]/Δt

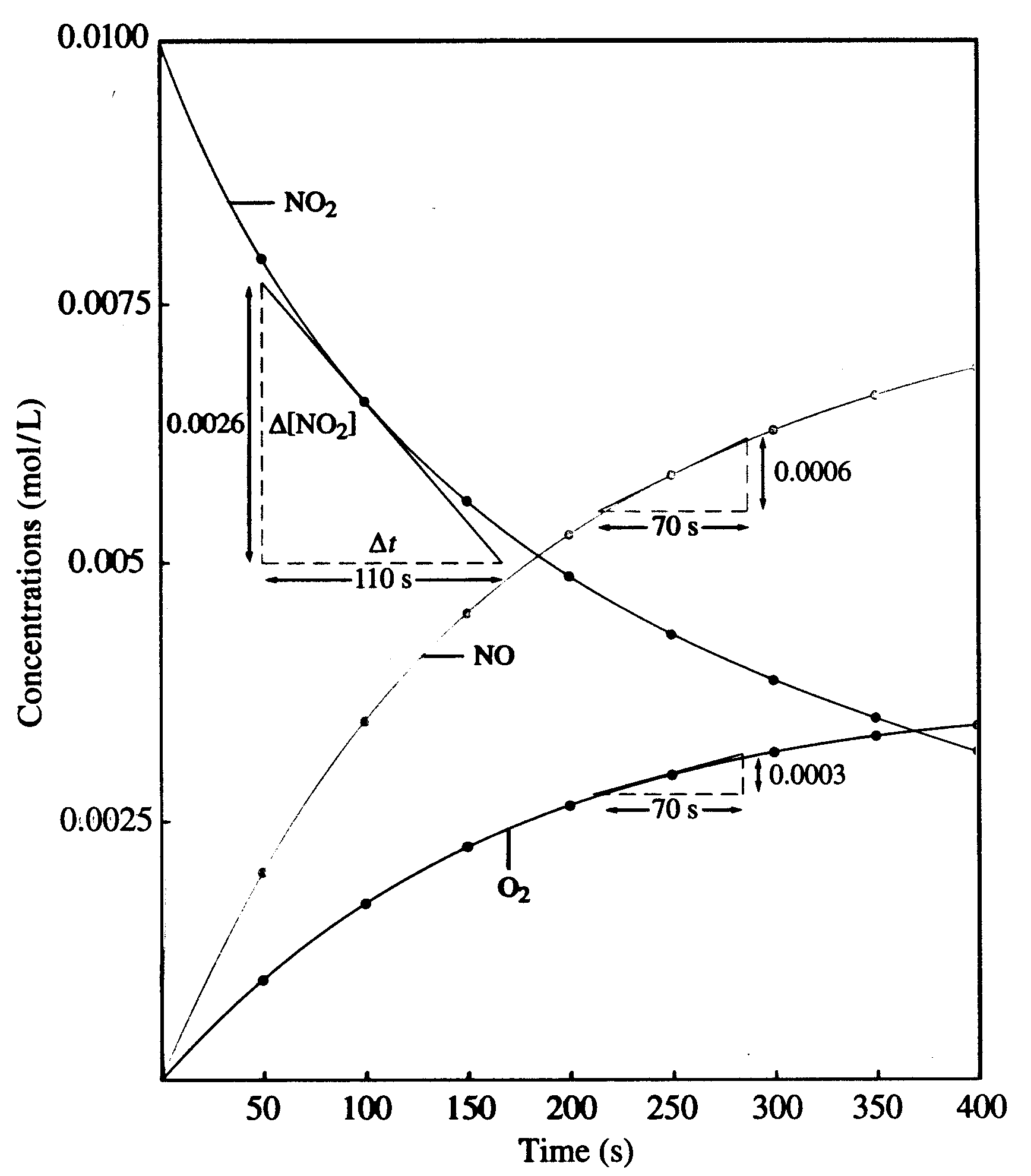
(Time may be in s, min., hr, even years.) ([ ] = molar concentration)

* A (-) sign shows in the calculations when using reactants because their concentration is decreasing but rates are always shown as (+) values.

Average rate= \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Instantaneous rate = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Given: 2NO2(g) 🡪 2NO(g) + O2(g)



# Reaction Rates and Stoichiometry

For the reaction of hydrogen and oxygen to give water,

2H2(g) + O2(g) 🡪 2H2O(l)

The rate of disappearance of H2 must be **twice** the rate for **O2**, and **equal** to the rate of appearance of **H2O**. This is because the **coefficients of the chemical equation tell you the relative rates**.

Consider : 2 NO2(g) 🡪 2 NO(g) + O2(g)

We could measure the disappearance of NO2 **or** the appearance of NO or O2.

-Δ[NO2]/Δt = Δ[NO]/Δt = 2Δ[O 2]/Δt

The \_\_\_\_\_\_ sign of Δ[NO2] means the substance is **disappearing.**

The 2 preceding Δ[O 2] tells us that \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Example:

2A + 3B 🡨🡪C + 4D

What is the rate of B,C, and D in reference to one mole of A?

Rate = - Δ[A] - Δ[B] Δ[C] Δ[D]

=

=

=

Δt Δt Δt Δt

**Rate Laws**

Reaction rate depends only on the concentration of the reactants (the reverse reaction will be neglected). A rate law shows how the rate depends on the concentrations of reactants.

rate =k[A]n k = rate constant

n = order

The [products] do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate. **The value of the exponent n must be determined by experiment; it cannot be written from the balanced equation**.

# Important: *k* will be the same value, no matter which set of data are used.

Use the method of initial rates to determine rate laws and rate constants. Let's consider the following example:

A + B 🡪 products

We want to determine a rate law for the decomposition of "A" that takes into account both [A] and [B]. We can hypothesize that the rate of the reaction is proportional to the concentrations of A and B. The more of each, the faster the reaction.

rate = ‑ Δ[A]/Δt = -Δ[B]/Δt = k[A]m[B]n

Gathering experimental data will allow us to determine the rate law. Our goal is to determine **x**, **y**, and **k**. The sum of the exponents, **m+ n**, is called the overall **reaction order**.

Zero order: r = k rate won’t change with concentration changes

First order in A: r = k[A] rate will change linearly with the concentration of A

(i.e. you double [A] the rate should double)

Second Order in A: r = k[A]2 rate will change as the square of a change in [A] (i.e. if you double [A] the rate will increase by a factor of 4)

In such a case, tripling the reactant concentration would

increase the reaction rate by \_\_\_times.

**KEY IDEA**: **Determining how the rate varies with varying concentration of one component while the concentration of the other is held constant.**

Problem:

Trial # [A]o [B]o Initial Rate of Reaction (M/s)

1 0.100 0.100 1.53 X 10-4

2 0.100 0.300 4.59 X 10-4

3 0.200 0.100 6.12 X 10-4

4 0.100 0.200 3.06 X 10-4

5 0.300 0.600 8.26 X 10-3

What happens to the rate when you vary [A]o while holding [B]o constant?

What happens to the rate when you vary [B]o while holding [A]o constant?

Determine the value of K.

**Problem:** Determine the rate law and solve for the order and value of the rate constant for the reaction

C + D + E 🡪 Products

given the following data:

Reaction # [C]o [D]o [E]o Initial Rate (M s‑1)

1 0.400 0.300 0.560 7.14 X 10-4

2 0.100 0.500 0.200 4.55 X 10-5

3 0.100 0.200 0.200 4.55 X 10-5

4 0.400 0.300 0.750 1.28 X 10-3

5 0.100 0.300 0.560 3.57 X 10-4

# Reaction Mechanisms

**Reaction Mechanism** - the sequence of *elementary steps* (generally **unimolecular** - one molecule splits apart) or mostly **bimolecular** - two molecules interact) which add up to the net reaction.

**Intermediate** - substance produced in one elementary step and used in a subsequent elementary step; intermediates cancel out in addition of steps.

**Molecularity** - the number of species that collide to produce the reaction indicated by the elementary step. Unimolecular and bimolecular are the two most important molecularities. Why not ternary?

**Rate-determining step** - the slowest step in the mechanism; the reaction can go only as fast as the slowest step.

**KEY IDEA:** The differential rate law is determined by the rate-determining step. This step may be in one direction or reversible. **For any elementary step in a mechanism you can use its stoichiometric coefficients as its rate order.** Our goal is to be able to determine whether mechanisms are consistent with experimentally determined rate laws. For the proposed mechanism to be consistent, the rate law of the slow step must match the observed rate law of the reaction. In writing the rate law of the slow step in the mechanism, it may be necessary to substitute for intermediates.

*Problem*: The balanced equation for the reaction of nitric oxide with hydrogen is:

2NO + 2H2 🡪 2H2O + N2

The experimentally determined rate law is

**rate = k[NO]2[H2**]

The following mechanism has been proposed,

NO + H2 🡪 N + H2O (slow)

k1

N + NO 🡪 N2O (fast)

k2

N2O + H2 🡪 N2 + H2O (fast)

k3

Is this mechanism consistent with the observed rate law?

There are two criteria that must be met if a mechanism is to be considered acceptable.

1. **The sum of the elementary steps must give the balanced equation**. If you add up the three steps, you will find that this is in fact true here.

2. **The mechanism must agree with the observed rate law**. According to the proposed mechanism, the first step is rate‑determining. This means that the overall mechanism must be given by the first step.

**rate = k1[NO][H2]**

This does not agree with the experimentally determined rate law, therefore our observed mechanism is incorrect.

Problem:

The rate law for the reaction shown is rate = k[ClO2][F2]

2ClO2(g) + F2(g) 🡪 2 ClO2F(g)

Which of the following reaction mechanisms is consistent with the rate law?

1. ClO2 + F2 🡪 ClO2F2 fast

ClO2F2 🡪 ClO2F + F slow

ClO2 + F 🡪 ClO2F fast

1. F2🡪 2F slow

2ClO2 +2 F 🡪 2ClO2F fast

Justify your answer

To review, in the Collision Model for Chemical Kinetics - molecules must collide to react:

1. Molecules must move toward each other.

2. Molecules must hit with proper orientation.

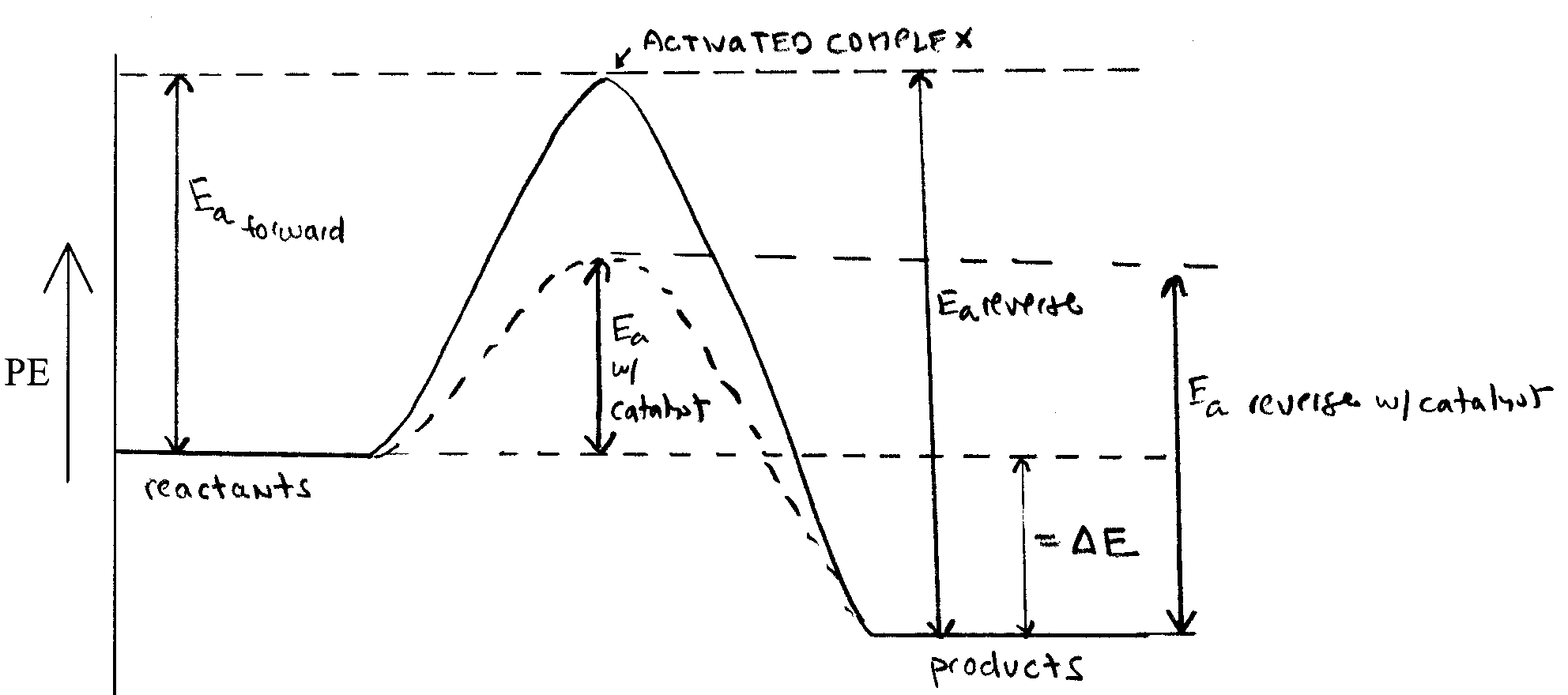
3. Molecules must hit with sufficiently high energy.

4. Molecules must separate after reaction occurs.

Numbers 2 and 3 make reaction unlikely. The odds of a collision are increased with higher concentration. The odds of collisions with sufficiently high energy are increased with increasing temperature.

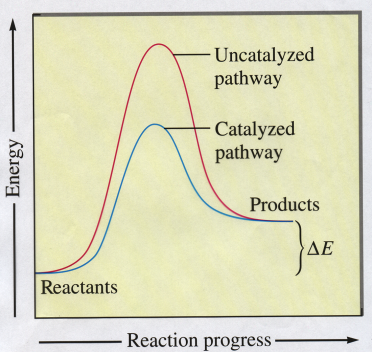
**Activation Energy (Ea)** = minimum of threshold energy needed to produce a reaction.

**Potential Energy Diagram:** for Reactants 🡪 Products + Energy

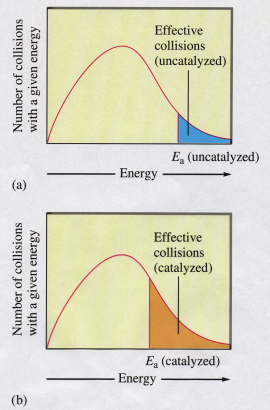


Time (min)

As two molecules approach each other they slow down due to electron cloud repulsions. Thus, their kinetic energies decrease. Since the total energy is conserved, this means their potential energy increases. At the moment the molecule hit and interact to form an activated complex (and are motionless for a billionth (?) of a second), all kinetic energy has been converted to potential energy. The product molecules then fly off, increasing the kinetic energy while decreasing the potential energy. The energy needed for the reactants to reach the activated complex is the activation energy (Ea). The net difference between the potential energies of the reactants and products is the heat of the reaction (∆H, or ∆E). Note that for an exothermic reaction the PE of the products is less than that of the reactants (and vice versa). Note also that adding a catalyst lowers the activation energy (by providing an alternate path – one requiring less energy) but has no effect on ∆H.



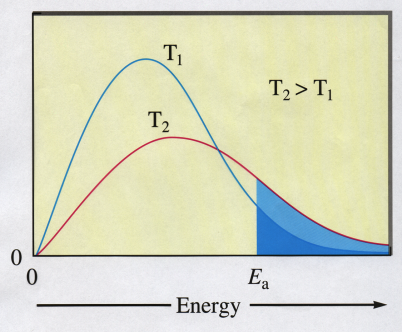
Below is another way to look at the effect of adding a catalyst:



Note that the result is a greater number of molecules having the required Ea to react.

The diagram below shows how increasing temperature effects the activation energy. The y axis refers to the total number of reacting molecules.

Number of molecules



Explain the above diagram:

Draw a rough potential energy diagram for a reaction having ΔH = -105 kJ with an Ea = 75 kJ/mol. On your diagram label the following:

* 1. PE of reactants
  2. PE of products
  3. ΔH
  4. PE of activated complex
  5. Ea of forward reaction
  6. Ea of reverse reaction

Use a dashed line to show how the diagram would be changed by the addition of a catalyst.

Demo 1

**Catalytic Decomposition of Hydrogen Peroxide**

**(Foam Production or Elephant Toothpaste)**

The rate of decomposition of hydrogen peroxide to water and oxygen gas can be greatly increased by the addition of potassium iodide as a catalyst. The net reaction is:

2 H2O2(aq) 🡪 2 H2O(l) + O2(g)

KI

It is believed the reaction involves a two-step mechanism:

1) H2O2(aq) + I-(aq) 🡪 H2O(l) + OI-(aq) (slow)

2) H2O2(aq) + OI-(aq) 🡪 H2O(l) + O2(g) + I-(aq)

Questions

1. What is the net reaction?
2. What is the molecularity of each step?
3. How does a catalyst work?
4. Which substance is the catalyst in this reaction? How do you know?
5. Was the catalyst used homogeneous or heterogeneous?
6. Identify the intermediate(s):
7. What happens to the KI?
8. How can you verify that oxygen gas was produced?

**The Oxidation of Tartaric Acid**

The oxidation of tartaric acid by hydrogen peroxide yields carbon dioxide and water. The rate can be increased by the addition of cobalt chloride. This demonstration is one of the few that allows one to actually observe the formation of an activated complex. The effect of temperature on the rate can also be easily demonstrated. The reaction is:

HC4H4O6(aq) + H2O2(aq) ----------> ----------> CO2(g) + H2O(l)

Co2+ Co-complex

pink green

Demo 3

**Oxidation of Baby Powder**

The efffect of surface area on the reaction is dramatically shown here!

Demo 4

**Catalytic Decomposition of Acetone**

In this reaction acetone, (CH3COCH3), catalytically decomposes on a hot copper surface to give a variety of products, the principle ones being ketene CH2CO and methane, CH4. Hot copper metal acts as a catalyst. Note in this reaction the copper is an example of a heterogeneous catalyst.

The copper is heated in a flame of a bunsen burner until it is glowing hot. The copper is suspended above a layer of acetone in a beaker. The copper continues to glow red hot due to the exothermic decopmposition of acetone. The reaction is:

CH3COCH3 🡪CH2CO + CH4

Cu